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by

D. E. Gragson and G. L. Richmond

Department of Chemistry
1253 University of Oregon
Eugene, OR 97403

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D. E. Gragson and G. L. Richmond

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University of Oregon
Eugene, OR 97403

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Comparisons of The Structure of Water at Neat Oil/Water and Air/Water Interfaces as Determined by Vibrational Sum Frequency Generation

D. E. Gragson and G. L. Richmond

Department of Chemistry, University of Oregon, Eugene, OR 97403

Abstract

We have employed vibrational sum frequency generation (VSFG) to measure for the first time the structure of water at the interface between two bulk immiscible liquids. The OH stretching modes of the interfacial water molecules are examined and compared with analogous studies at the air/water interface. We find that at the oil/water interface the prevailing structure of the water molecules is a tetrahedral arrangement much like the structure of ice, while at the air/water interface we observe an equal distribution between an ice-like and a less ordered water-like arrangement. The relationship between the structure of the interfacial water molecules and the properties of the other fluid (air or oil) is discussed in terms of hydrogen bonding at the interface. We also compare our results to previous VSFG studies and find that our spectrum obtained from the CCl_4/water interface differs from what was obtained by others at the hexane/water interface.

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Introduction

There are numerous examples of processes that are affected by the structural features of interfacial water molecules.[1] Among the most important are solvent extraction, charge transfer across liquid/liquid interfaces, stability of membranes and the activity of proteins in an aqueous environment. In recent years an increasing amount of experimental[2-7] and theoretical[8-11] work has been performed in an effort to better understand the structure of water molecules at a variety of interfaces. We have employed vibrational sum frequency generation (VSFG) to measure for the first time the structure of water at the interface between two bulk immiscible liquids. The OH stretching modes of the interfacial water molecules are examined and compared with analogous studies at the air/water interface. Our studies show a striking difference between the VSFG spectra obtained from these interfaces. From this difference we infer that nominally all of the water molecules at the oil/water interface are in a tetrahedral arrangement much like the structure of ice, whereas at the air/water interface only about 60% of the water molecules are in the same arrangement with the remaining water molecules being in a more random and bond-disordered arrangement presumed to be more water-like. This observation is explained in terms of the structural changes liquid water must make in order to solvate non-polar oil molecules.

The VSFG process has been explained in detail elsewhere[4,12,13] thus the only the most important aspects will be discussed here. First, under the dipole approximation VSFG is inherently interface selective due to the fact that it is a second order nonlinear process. Second, VSFG allows us to obtain a vibrational spectrum of the interfacial molecules. This capability arises from the fact that the sum frequency response is proportional to the square of the material dependent nonlinear susceptibility $\chi^{(2)}$. $\chi^{(2)}$ can be

separated into a non-resonant, χ_{NR}, and resonant, χ_{Rv}, portion, the former being independent of IR frequency while the latter depends on IR frequency as follows

$$I_{sfg} \propto \left| \chi_{NR}^{(2)} + \sum_{v} \left| \chi_{R_v}^{(2)} \right| e^{i\gamma_v} \right|^2 I_{vis}I_{ir}.$$ (1)

I_{sfg} is the sum frequency intensity generated at ω_{sfg}, γ_v is the relative phase of the vth vibrational mode, I_{vis} and I_{ir} are the visible and IR intensities, and the sum is taken over all vibrational modes v of the molecules at the interface. Since the susceptibility is in general complex the resonant terms in the summation are associated with a relative phase γ_v which is used to account for any interference between two modes which overlap in energy. The resonant portion of $\chi^{(2)}$ can be expressed such that the dependence on the IR frequency is apparent,

$$\chi_{R_v}^{(2)} \propto \frac{A_v}{\omega_v - \omega_{ir} - i\Gamma_v}.$$ (2)

A_v is the intensity of the vth mode and is proportional to the product of the Raman and the IR transition moments, ω_v is the resonant frequency, and Γ_v is the line width of the transition. Equations 1 and 2 show that there is an enhancement in $\chi^{(2)}$ and I_{sfg} as the IR frequency is tuned through allowed vibrational resonances of molecules present at the interface. In this way VSFG provides a means to obtain vibrational spectra of interfacial molecules without the complication of interfering bulk material.

Experimental

The laser system employed for the vibrational SFG studies has been described in detail elsewhere.[14] Briefly it consists of a titanium:sapphire regenerative amplifier which pumps a two-stage optical parametric amplifier seeded with a small portion of white light

continuum. The system produces IR pulses tunable from 2.4 μm to 4.0 μm at a repetition rate of 1 kHz. The energy of the pulses over this range is approximately 10 μJ with a bandwidth of 18 cm^{-1} and a pulse duration of 1.9 ps. The IR pulses are combined at the interface with approximately 150 μJ of 800 nm light from the Ti:sapphire regenerative amplifier. All spectra presented were obtained under S_{sfg}, S_{vis}, P_{ir} polarization conditions which picks out the vibrational modes with components of the transition dipole moment perpendicular to the plane of the interface. Spectra of the air/water interface were obtained in an external reflection geometry[3,4] with the 800 nm and tunable IR beams coincident on the interface at angles of 56 and 68 degrees from the surface normal respectively. Spectra from the CCl$_4$/water interface were obtained in an internal reflection geometry[12,15] with the 800 nm and tunable IR beams coincident on the interface from the CCl$_4$ side at the critical angle for each wavelength (66.5 and 73.2 degrees respectively). In each case the generated sum frequency light is detected in reflection with a PMT after filtering. Individual spectra were collected with gated electronics and a computer while the IR frequency was scanned from 2850 cm^{-1} to 3700 cm^{-1}. Each scan was obtained with an increment of 4 cm^{-1} and an average of 300 laser shots per increment and each spectra presented is an average of at least two scans. Both 18 MΩ water from a Nanopure filtration system and HPLC grade water from Mallinckrodt were used with no detectable difference in the VSFG spectra. 99.9+% HPLC grade carbon tetrachloride from Sigma-Aldrich was used as received. Absorption of the tunable IR beam in the OH stretching region by the CCl$_4$ was determined to be negligible with FTIR and by monitoring the IR energy after the beam had traversed a 1 cm path length of CCl$_4$.

Results and Discussion

The VSFG spectra from the neat air/water and CCl$_4$/water interfaces are shown in Figure 1. Table 1 lists the data obtained from fitting each spectra to a Lorentzian according

to Equations 1 and 2. There are two peaks of primary interest to the work presented here. The first peak (OH-SS-S) occurs at 3200 cm^{-1} and is attributed to the in-phase vibrations of the coupled OH symmetric stretching mode of tetrahedrally coordinated water molecules. This peak has been shown[3,6,13] to be indicative of a high degree of bond ordering and an ice-like structure in the molecular arrangement of the water molecules. The second peak (OH-SS-A) occurs at approximately 3400 cm^{-1} and two different modes have been suggested for this peak. The first assignment[3,6,13] is the OH symmetric stretch from water molecules that are asymmetrically hydrogen bonded or in a more random and water-like molecular arrangement. Other authors have attributed this peak to the OH stretch from water molecules with bifurcated hydrogen bonds,[16] this assignment also implies a molecular arrangement with a higher degree of bond disorder than the OH-SS-S peak. Since both OH-SS-A peak assignments imply a higher degree of bond disorder than the OH-SS-S peak the relative number of water molecules in an ice-like or a water-like arrangement can be determined through analysis of the VSFG spectra. The small peak observed at approximately 2950 cm^{-1} in the VSFG spectrum from the CCl$_4$/water interface is a result of a very small amount of contaminant at the interface. Both the air/water and oil/water interfaces are prepared from the same materials and all glassware and experimental equipment is cleaned with the same procedure. The fact that a small amount of contaminant is visible in the VSFG spectrum from the CCl$_4$/water interface and not the air/water interface is a result of the enhancement in the VSFG signal obtained in the total internal reflection (TIR) geometry which we have found from previous studies[12] to be as much as four orders of magnitude. In fact, from our studies of surfactants at oil/water interfaces we have been able to detect surface concentrations as small as a thousandth of maximum surface coverage which corresponds to a molecular area of approximately 1500 Å^2/molecule. Adding to our increased sensitivity in the TIR geometry is the fact that many trace bulk impurities will preferentially adsorb at the oil/water interface and thus result in small signals in the VSFG spectrum.

Analysis of the spectra in Figure 1 shows that the structure of the interfacial water molecules at the oil/water interface differs markedly from the structure at the air/water interface. Namely, at the oil/water interface the VSFG spectrum is dominated by the OH-SS-S peak with no evidence of the OH-SS-A peak whereas at the air/water interface there is clear evidence of both peaks in the VSFG spectrum. The relative number of water molecules contributing to each peak can be determined by taking the square root of the integrated intensity for each peak and dividing that into the sum of the square root of the integrated intensity for the two peaks. At the oil/water interface we find that essentially all the water molecules are in an ice-like arrangement while at the air/water interface we find that only about 60% of the water molecules are in an ice-like arrangement with the remaining water molecules in a more bond disordered water-like arrangement. This difference can be explained in terms of the ability of water to solvate a non-polar molecule such as CCl_4 and the corresponding decrease in entropy associated with the solvation of non-polar molecules.[1,17,18] It is this decrease in the entropy of the system which over rides the enthalpy of solvation and causes the solvation of non-polar molecules in water to be energetically unfavorable. The decrease in entropy is thought to result from water molecules rearranging into a tetrahedral structure in order to maximize hydrogen bonding in the presence of a non-polar solute.[1,18] Our observation that the VSFG spectrum is dominated by the ice-like peak at the CCl_4/water interface is a direct manifestation of the structure inducing influence of CCl_4 molecules on the interfacial water molecules. This observation is also consistent with previous calculations of hydrogen bonding at an oil/water interface which suggest that there is an increase in the strength of the hydrogen bonding among the water molecules near a hydrophobic surface.[8] At the air/water interface the water molecules are not influenced by the presence of a non-polar molecule and thus the water-like peak accompanies the ice-like peak. For the air/water interface the ice-like character is a result of bulk termination which induces maximum formation of hydrogen bonds at the interface and thus the tetrahedral structure is preferred.

The VSFG spectrum that we have obtained from the air/water interface is in good agreement with previous VSFG work by Shen *et. al.*.[2] However, our CCl_4/water results differ from what they observe from the presumably similar hexane/water interface. Shen *et. al.* found that at the air/water and hexane/water interfaces the VSFG spectra were very similar in that there was nominally an equal distribution of intensity between the water-like and ice-like modes. This observation differed from the quartz/octadecyltrichlorosilane(OTS)/water interface where they found that the VSFG spectrum was dominated by the ice-like mode. Since each of these interfaces was determined to be hydrophobic as evidenced by the observation of the non-hydrogen bonded peak in the VSFG spectra at approximately 3680 cm^{-1} their explanation of the difference was based on the rigidity of the interface. Namely, that at the quartz/OTS/water interface the rigid quartz-OTS wall forces the surface water molecules into the more orderly ice-like structure because of the physical restriction involved in packing molecules against the wall. At the air/water and hexane/water interfaces which exhibit the same hydrophobicity, this rigid wall is not present and thus the water molecules are less bond-ordered and the water-like peak is present in the VSFG spectra.

Our observation that the VSFG spectrum from the CCl_4/water interface is dominated by the OH-SS-S or ice-like peak agrees well with VSFG spectra obtained at the rigid hydrophobic quartz/OTS/water interface indicating that these two interfaces may be similar. The observed difference in the water structure for CCl_4/water compared to what has been observed previously for hexane/water suggests a very different local environment for the interfacial water molecules at these two different interfaces. This discrepancy is either due to inherent differences in the interaction of water with CCl_4 and alkanes or is possibly due to the difference in the thickness of the organic phases. The aforementioned VSFG spectrum from the hexane/water interface was obtained by spreading a thin layer of hexane on the water surface and then recording a spectrum. For our studies at the CCl_4/water interface approximately 50 mL of water is placed on top of 180 mL of CCl_4.

One might argue that there could be an increase in the rigidity due to the hydrostatic pressure of 50 mL of water pushing down on the interface thus restricting the packing of the water molecules. This explanation seems to contradict theoretical[8-10] and experimental[19,20] endeavors from which a high degree of interface roughness at these interfaces is inferred. We have attempted to perform similar experiments using hexane and cyclohexane and have been unsuccessful in obtaining reliable spectra from these interfaces. The main experimental complication has been absorption of the IR light by the thin layer of alkane thus rendering the IR light that reaches the interface too weak to produce a detectable VSFG response.

Conclusions

In summary, we have employed VSFG to investigate the molecular arrangement of water molecules at both the oil/water and the air/water interface through OH stretching modes that are sensitive to the hydrogen bonding environment. From our spectra we infer that the water molecules at an oil/water interface are predominantly in a tetrahedral arrangement similar to that of ice. This conclusion is different from what is observed at the air/water interface where only approximately 60% of the water molecules were found to contribute to the ice-like stretching mode. The difference in the behavior of the interfacial water molecules is a direct consequence of structure imposing effects caused by interactions between the non-polar CCl_4 molecules and the water molecules. This structural information gives us a better understanding of the properties of these technologically and biologically relevant interfacial systems and in the future may be extended to help explain such processes as solvent extraction and charge transfer.

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References

1)Jones, M. N.; Chapman, D. *Micelles, Monolayers, and Biomembranes*; ; Wiley-Liss: New York, 1995.

2)Du, Q.; Freysz, E.; Shen, Y. R. *Science (Washington, D. C.)* **1994**, *264*, 826-8.

3)Gragson, D. E.; McCarty, B. M.; Richmond, G. L. *J. Phys. Chem.* **1996**, *100*, 14272-14275.

4)Gragson, D. E.; McCarty, B. M.; Richmond, G. L. *J. Am. Chem. Soc.* **1997**, *In Press.*

5)Toney, M. F.; Howard, J. N.; Richer, J.; Borges, G. L.; Gordon, J. G.; Melroy, O. R.; Wiesler, D. G.; Yee, D.; Sorensen, L. B. *Nature* **1994**, *368*, 444-446.

6)Yalamanchili, M. R.; Atia, A. A.; Miller, J. D. *Langmuir* **1996**, *12*, 4176-4184.

7)Zhao, X.; Ong, S.; Eisenthal, K. B. *Chem. Phys. Lett.* **1993**, *202*, 513-520.

8)Michael, D.; Benjamin, I. *J. Phys. Chem.* **1995**, *99*, 1530.

9)Carpenter, I. L.; Hehre, W. J. *J. Phys. Chem.* **1990**, *94*, 531.

10)Benjamin, I. *Chem. Rev.* **1996**, *96*, 1449-1475.

11)Schweighofer, K. J.; Xia, X.; Berkowitz, M. L. *Langmuir* **1996**, *12*, 3747-3752.

12)Conboy, J. C.; Messmer, M. C.; Richmond, G. L. *J. Phys. Chem.* **1996**, *100*, 7617-7622.

13)Du, Q.; Superfine, R.; Freysz, E.; Shen, Y. R. *Phys. Rev. Lett.* **1993**, *70*, 2313-16.

14)Gragson, D. E.; McCarty, B. M.; Richmond, G. L.; Alavi, D. S. *J. Opt. Soc. Am. B* **1996**, *13*, 2075-2083.

15)Messmer, M. C.; Conboy, J. C.; Richmond, G. L. *J. Am. Chem. Soc.* **1995**, *117*, 8039-40.

16)Giguere, P. A. *J. Raman Spec.* **1984**, *15*, 354-359.

17)Eisenberg, D.; Kauzmann, W. *The Structure and Properties of Water*; ; Oxford University Press: New York, 1969.

18)Tanford, C. *The Hydrophobic Effect*; ; Wiley-Interscience: New York, 1973.

19)Kovaleski, J. M.; Wirth, M. J. *J. Phys. Chem.* **1995**, *99*, 4091.

20)Wirth, M. J.; Burbage, J. D. *J. Phys. Chem.* **1992**, *96*, 9022.

Figure and Table Captions

Table 1

Spectral assignments and data obtained from fit of experimental data to Equations 1 and 2 along with OH stretching mode data obtained from Reference 12.

Figure 1

VSFG spectra under S-sfg, S-vis, P-ir polarization conditions from the neat CCl_4/water (open circles) and air/water (filled circles) interfaces. Solid lines are a fit to Equations 1 and 2.

Table 1

Interface	Peak Frequency (cm^{-1})	Integrated Area (a.u.)	Peak FWHM (cm^{-1})
OH-SS-S, O/W, This study	3200	300	277
OH-SS-A, O/W, This study	3400	N/A	N/A
OH-SS-S, A/W, This study	3206	90	276
OH-SS-A, A/W, This study	3417	41	180
OH-SS-S, A/W, Ref. (13)	3257.5	N/A	217.2
OH-SS-A, A/W, Ref. (13)	3451.3	N/A	203
Free-OH, A/W, Ref. (13)	3682.9	N/A	66.6

Figure 1